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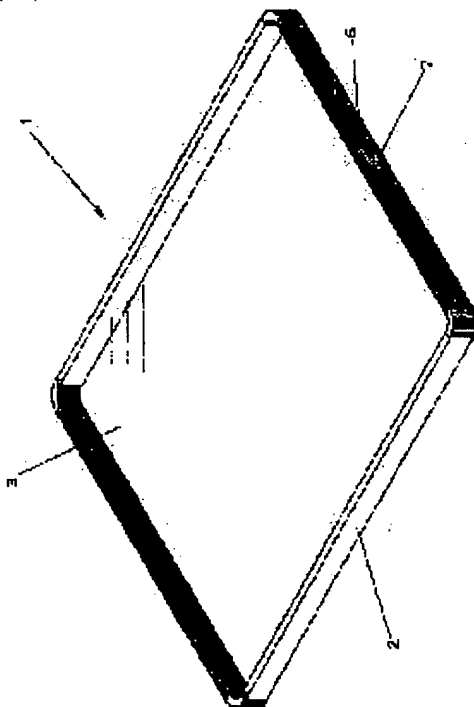
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## (54) PELLICLE FOR LITHOGRAPHY



(57)Abstract:

PROBLEM TO BE SOLVED: To provide a pellicle which eliminates influences of pollutant gas as such as organic gas present in the exposure environment and which can respond to semiconductor lithography with shorter wavelengths.

SOLUTION: The pellicle film for lithography is produced by adhering a pellicle film to at least a pellicle frame. The pellicle frame 2 has a ventilation port 6 and is provided with a dust collecting filter and a chemical filter on the ventilation port. A filter containing titanium oxide is preferably used for the chemical filter.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the pellicle for lithography used as dust \*\*\*\* of the mask for lithography at the time of manufacturing a semiconductor device or liquid crystal display panels, such as LSI and a VLSI.

[0002]

[Description of the Prior Art] Although light is irradiated and patterning is performed to a semiconductor wafer or the negative for liquid crystal in semi-conductor manufacture of LSI, a VLSI, etc., or manufacture of a liquid crystal display panel etc. In this case, if dust has adhered to the exposure negative (generally called "the mask for lithography", or a "reticle") to be used, in order for this dust to absorb light or to bend light The imprinted pattern deforms, or an edge becomes an ill-behaved \*\*\*\* thing, and also a substrate will become dirty black and a dimension, quality, an appearance, etc. will be spoiled.

[0003] For this reason, although the activity about such lithography is usually done in the clean room, since it is difficult to always maintain an exposure negative at clarification also in this clean room, the approach of sticking on the front face of an exposure negative the pellicle which makes the light for exposure for dust \*\*\*\* often penetrate is taken. In this case, since dust does not adhere directly on the front face of the exposure original edition but it adheres on the pellicle film, if the focus is doubled on the pattern of the exposure original edition at the time of lithography, the dust on the pellicle film will become unrelated to an imprint.

[0004] Drawing 1 shows the fundamental configuration of a pellicle. Such pellicle 1' applies the good solvent of the pellicle film 3 to the upper limit side of the pellicle frame 2 which consists the transparent pellicle film 3 which consists of a nitrocellulose which makes the light used for exposure penetrate well, cellulose acetate, etc. of aluminium alloys, such as A7075 which performed black alumite processing, stainless steel, polyethylene, etc., and is air-dry and pastes up, or (refer to JP,58-219023,A) is pasted up with adhesives, such as acrylic resin and an epoxy resin, (refer to a U.S. Pat. No. 4861402 specification and JP,63-27707,B). Furthermore, the liner 5 for reticle binder protection aiming at protection of the adhesive layer 4 which consists of the polybutene resin for equipping the exposure original edition, polyvinyl acetate resin, acrylic resin, etc., and an adhesive layer 4 is formed in the lower limit side of the pellicle frame 2.

[0005] In case it exposes, a pellicle is installed so that the pattern space formed in the front face of a mask substrate may be surrounded, but a pellicle is for preventing that dust adheres on a mask substrate (reticle), as described above, and if it puts in another way, a pattern space needs to be isolated so that the dust of the pellicle exterior may not adhere to a pattern side. Therefore, the sealed pellicle without permeability has been used conventionally.

[0006] However, if it will be sealed [ the pattern formation side of a mask (reticle) ] by the pellicle in this way For example, if a reticle is conveyed to the works of high ground where a pellicle is stuck on a mask side, or a low pressure approaches, since the atmospheric pressure of an ambient atmosphere will fall, The pellicle film swelled and

there was a problem of the pellicle film contacting some equipments for exposure, or the focus of the laser for lighting having shifted and incorrect-detecting in case dust particle inspection of a pellicle film surface is conducted.

[0007] In order to solve such a problem, while preparing a bleeder in the side face of a pellicle frame, a filter is prepared in the outside of a bleeder and the pellicle which can perform pressurization is proposed (for example, refer to JP,61-41255,U). Moreover, the pellicle which gave adhesive resin to the interior of a small bleeder established in the pellicle frame is proposed (refer to JP,2-250055,A). Each of these pellicles does so the effectiveness of losing the differential pressure of pellicle inside and outside while preventing invasion of foreign matters, such as dust.

[0008]

[Problem(s) to be Solved by the Invention] By the way, detailed-ization is progressing to the subquarter micron, and, as for the pattern rule of LSI, much more short wavelength-ization of the exposure light source is progressing in connection with it in recent years. namely, the KrF excimer laser (248nm) from g line (436nm) by the mercury lamp which was in use until now, or i line (365nm) and an ArF excimer laser (193nm) -- F2 laser (157nm) etc. is being used further. If short wavelength-ization of such exposure progresses, the energy which exposure light naturally has will become high.

[0009] when using the light of the above high energy, compared with the light with comparatively long wavelength currently used conventionally, it is easy to trigger the reaction of the gaseous substance which exists in an exposure ambient atmosphere, and possibility of generating a resultant is markedly alike and becomes high. Then, the gaseous substance in a clean room is reduced as much as possible, or the measures of eliminating what emits gas from the constituent of a pellicle have been taken. However, such a cure might take immense costs, or effectiveness also seldom went up, and it was not realistic.

[0010] So, in this invention, the effect of contamination gas, such as organic gas which exists in an exposure environment, is eliminated, and it aims at offering the pellicle which can respond also to the semi-conductor lithography with which short wavelength-ization progresses more.

[0011]

[Means for Solving the Problem] In order to attain this purpose, this invention persons find out that the contamination gas removal in a closed space between a pellicle and a reticle can also be performed, and complete this invention while they prevent invasion of the contamination gas from the outside by preparing the chemical filter other than the filter for dust removing in the bleeder formed in the pellicle frame, as a result of stepping up examination efforts wholeheartedly.

[0012] That is, according to this invention, it is the pellicle for lithography which comes to paste a pellicle frame the pellicle film at least, and while said pellicle frame has a bleeder, the pellicle for lithography characterized by preparing the filter for dust removing and the chemical filter in this bleeder is offered (claim 1).

[0013] Although there was a pellicle which measured dust removing with aeration by equipping with the filter for dust removing conventionally the bleeder prepared in the frame side face as described above, in the pellicle of this invention, in addition to the dust-removing effectiveness, adsorption, decomposition, etc. can be carried out and providing a chemical filter further can remove contamination gas. Therefore, since

contamination gas etc. is removed also in case it exposes with the light of short wavelength more if the pellicle of this invention is used in semi-conductor lithography, generating of the sludge from gas can be prevented and a very detailed pattern can be made to form suitably on a substrate as a result.

[0014] It is desirable that a chemical filter is a thing containing titanium oxide (claim 2). By using the chemical filter containing such titanium oxide, contamination gas, such as organic gas, can be removed more effectively.

[0015] Furthermore, it is desirable to coat with titanium oxide the fiber of the thing which scoured titanium oxide to polytetrafluoroethylene, or an inorganic material as a chemical filter containing titanium oxide (claim 3). If it is the titanium oxide content chemical filter of such a gestalt, it can produce comparatively easily and the contamination gas-removal effectiveness can be demonstrated enough.

[0016] It is desirable that said filter for dust removing is what consists of fluororesin, a metal, or ceramics (claim 4). If the filter for dust removing which consists of such the quality of the material is used, it can prevent deteriorating, even if it receives the oxidation by the titanium oxide contained in the chemical filter, while having sufficient dust-removing effectiveness.

[0017]

[Embodiment of the Invention] Hereafter, this invention is further explained to a detail, referring to an accompanying drawing. Drawing 2 shows an example of the pellicle concerning this invention, and drawing 3 shows an example of the filter concerning this invention. At least one bleeder is formed in at least 1 side face of a pellicle frame, and the pellicle of this invention is characterized by preparing the filter for dust removing, and a chemical filter in this bleeder. In the pellicle 1 of drawing 2, one rectangle-like bleeder 6 is formed in the center of abbreviation of one side face.

[0018] What is necessary is just to choose the size, a configuration, the number, and a location with the quantity of airflow calculated from the mesh size of the filter installed in a bleeder, a filtration area, or these, although there is especially no limit about the size of a bleeder, a configuration, the number, and a location. It is good not to form the desirable big bleeder beyond the need, but to form the bleeder which secures the aeration of the need minimum amount.

[0019] The filter collection object 7 of drawing 3 carries out the laminating of the thing which the chemical filter 9 which contains a titanium oxide layer in the protection networks 10a and 10b which consist of organic fiber or an inorganic fiber was made to \*\*\*\* to the filter 8 for dust removing, and is constituted. Moreover, the pressure sensitive adhesive double coated tape 11 is stuck on the periphery of the opposite side of the filter 8 for dust removing, and by minding this pressure sensitive adhesive double coated tape 11, the filter collection object 7 can be established, as the bleeder 6 of the pellicle frame 2 is covered. In addition, as long as the structure of the filter concerning this invention is not limited to the thing of drawing 3 but can demonstrate the same effectiveness, what kind of structure is sufficient as it.

[0020] Although the thing containing activated carbon, activation activated carbon, or ion-exchange resin can be used for a chemical filter that what is necessary is just to decide suitably according to the gas to remove, its thing containing titanium oxide is [ the filter which has a titanium oxide layer especially ] desirable. Thus, if it is the chemical filter of titanium oxide content, contamination gas, such as organic gas, is effectively

removable with adsorption and decomposition.

[0021] Especially the gestalt of the chemical filter containing such titanium oxide is not limited, either, but a titanium oxide layer is formed in the front face of organic fiber with the thing which made fiber etc. contain titanium oxide, or the detailed hole which forms the filter for dust removing, or an inorganic fiber, and it is good also as the filter for dust removing, and what [ one-/ a thing ].

[0022] What coated with titanium oxide the fiber which specifically becomes polytetrafluoroethylene from inorganic materials, such as a thing which scoured titanium oxide, or ceramics, with the sol gel process can be used. If it is such a chemical filter, when the contamination gas-removal effectiveness can be demonstrated enough, it can produce comparatively easily. In addition, it is not limited to especially the above-mentioned thing about the formation approach of a chemical filter.

[0023] By preparing such a chemical filter in the bleeder of a frame, while preventing effectively that organic [ from the pellicle outside ] and various inorganic gas invade in a pellicle, the gas which is enclosed at the time of pellicle attachment and exists in a pellicle is removable at the time of aeration. That is, since an internal gas removal can be performed while preventing invasion of the contamination gas into the closed space of a pellicle and a reticle, generating and the deposit of a foreign matter which originate in gas under the lithography environment of high energies, such as ArF and F2 laser, can be prevented.

[0024] As a filter 8 for dust removing, if it can install in bleeder 6 part of a frame 2, there will be especially no limit in a configuration, the number, and a location. Moreover, as the quality of the material of the filter for dust removing, resin (PTFE, Nylon 66, etc.), metals (316L stainless steel etc.), ceramics (an alumina, aluminum nitride, etc.), etc. are mentioned. However, if what contains titanium oxide as a chemical filter is used for the lateral part of the filter for dust removing, the quality of the material of the filter for dust removing needs to be what does not deteriorate even if it receives the oxidation by titanium oxide. Therefore, ceramics, such as metals, such as fluororesin, such as PTFE (polytetrafluoroethylene), and 316L stainless steel, an alumina, and aluminum nitride, is desirable preferably.

[0025] In addition, it is desirable to \*\*\*\* a chemical filter outside for the filter for dust removing to the inside (closed-space side) in this invention. By carrying out like this, a chemical filter serves as a source of raising dust, and dust does not trespass upon the closed space of a pellicle.

[0026] The pellicle of this invention can be made into the same thing as general pellicle 1' shown in drawing 1 except equipping the pellicle frame with the bleeder, the filter for dust removing, and the chemical filter. That is, the magnitude of other members which constitute the pellicle of this invention is the same as that of the usual pellicle, and can be made into the well-known quality of the material which also mentioned above the quality of the material. As shown in drawing 1, the pellicle film 3 is stretched through the adhesives for pellicle film attachment to the upper limit side of the pellicle frame 2, the binder 4 for reticle adhesion is formed in the lower limit side of a frame 2, and, specifically, the liner 5 for protection is usually stuck on the lower limit side of the binder 4 for reticle adhesion possible [ exfoliation ].

[0027] For example, about the pellicle film, the amorphous fluorine polymer currently used for the conventional excimer lasers is used. As an example of an amorphous fluorine

polymer, SAITOPPU (trade name by Asahi Glass Co., Ltd.), Teflon AF (trade name by E. I. du Pont de Nemours & Co.), etc. are mentioned. These polymers may be used for a solvent if needed at the time of the pellicle film production, dissolving, for example, may be suitably dissolved with a fluorine system solvent etc.

[0028] Moreover, there is especially no limit also about the quality of the material of a pellicle frame, and blue plate glass, quartz glass, etc. are mentioned to synthetic resin, such as what performed anodizing to the aluminum material currently used conventionally, stainless steel or polyacetal, a polycarbonate, PMMA (polymethylmethacrylate), and acrylic resin, and a pan.

[0029] Although usually roughened by sandblasting or chemical polishing about a pellicle frame front face, in this invention, constraint is not given at all about roughening on this front face of a frame. For example, when aluminum material is used, blasting processing of the front face is carried out with stainless steel, a Carborundum, a glass bead, etc., the approach of performing chemical polishing by NaOH etc. and roughening a front face is learned further, and this can be applied.

[0030] Although the conventional thing can be used, for example, fluorine system polymers, such as polyacrylate adhesive, epoxy resin adhesive, silicone resin adhesives, and fluorine-containing silicone adhesives, etc. can be mentioned as adhesives for pellicle film adhesion, a fluorine system polymer is suitable especially. As a fluorine system polymer, the fluorine system polymer CT 69 (trade name by Asahi Glass Co., Ltd.) is specifically mentioned.

[0031] In addition, the adhesives layer for pellicle film attachment formed in a pellicle frame upper limit side can be diluted with a solvent as occasion demands, and can be formed by applying and heating, drying to a pellicle frame upper limit side, and stiffening it. In this case, as the method of application of adhesives, the approach by brush coating, the spray, and the automatic dispenser etc. is employable.

[0032] As adhesives for reticle attachment, a pressure sensitive adhesive double coated tape, a silicone resin binder, an acrylic binder, etc. can be mentioned.

[0033] About the liner for reticle adhesives protection, if used conventionally, especially the quality of the material will not be restricted, for example, PET, PTFE, PFA, PE, PC (polycarbonate), vinyl chloride, PP, etc. will be mentioned.

[0034] And about set-up of the pellicle film etc., the pellicle film can be stretched through the adhesives layer for pellicle film attachment to the upper limit side of a pellicle frame by the usual approach, and the adhesives layer for reticle attachment can usually be formed in the lower limit side of a frame, and it can consider as a pellicle by sticking a mold release layer (liner for protection) possible [ exfoliation ], and making it further, the inferior surface of tongue of this adhesives layer for reticle attachment.

[0035]

[Example] Although an example and the example of a comparison are shown and this invention is explained more concretely hereafter, this invention is not limited to these.

[0036] (Example)

As a pellicle frame, the frame made from an aluminium alloy with a \*\* 149mmx122mmx5.8mm and a frame thickness of 2mm was prepared frame outside, and the hole with a diameter of 0.5mm was prepared in the center of 1 side face of a frame as a bleeder at the beginning of <production of a pellicle frame>.

[0037] After carrying out surface washing of this frame, the glass bead was used with the

sandblast cleaning machine, surface treatment was performed for 1 minute with the discharge pressure of 1.5kg/cm<sup>2</sup>, and the front face was roughened. Subsequently, after washing this for 10 seconds in a NaOH processing bath, it anodized and black-dyed, and sealing was carried out and the black oxide skin was formed in the front face. Furthermore, this aluminum frame was washed using pure water and an ultrasonic cleaner. Subsequently, spray coating equipment was used for the inside of this frame, and the silicone system binder was coated with about 1 micrometer in thickness. [0038] Next, dust filtration size installed the filter with a height [ width of face of 9.5mm and height of 2.5mm ] whose quality of the material is 99.9999% in PTFE, and a thickness of 300 micrometers in the bleeder of a frame by 0.1 micrometers - 3.0 micrometers. The structure of this filter carries out the laminating of the titanium oxide content layer as a chemical filter to the outside of the filter for dust removing as shown in drawing 3.

[0039] <Production of pellicle film> Teflon AF 1600 (trade name by U.S. Du Pont) was dissolved in a fluorine system solvent and FURORINATO FC-75 (U.S. three em company trade name), and the solution of 8% of concentration was prepared. The spin coater was used for the silicon substrate side with a diameter [ of 200mm ], and a thickness of 600 micrometers which carried out mirror polishing, and the transparent membrane whose thickness is 0.8 micrometers was made to form in it using this solution. [0040] Furthermore, outside, epoxy system adhesives Araldite rapid (trade name by Showa High Polymer Co., Ltd.) was used for this film, the frame (frame for preparation) with \*\* 200mmx200mm, a width of face [ of 5mm ], and a thickness of 5mm was pasted up on it, and the film was underwater exfoliated from the silicon substrate.

[0041] A silicone system binder is applied to the end side of the pellicle frame made from an aluminium alloy which is the <production of pellicle> above, and was made and prepared as adhesives for reticle attachment, at 100 degrees C, it heated for 10 minutes and desiccation hardening was carried out. Moreover, the fluorine system macromolecule polymer CTX (Asahi Glass trade name) diluted to fluorine system solvent CT SORUBU 180 (Asahi Glass trade name) is applied as an object for pellicle film adhesion on the end face of the opposite side of this frame, at 100 degrees C, it heated for 10 minutes and desiccation hardening was carried out. Furthermore, the liner made from PET is prepared and it stuck on reticle adhesives with the liner attachment equipment which has an image-processing positioning device by the CCD camera.

[0042] Next, it produces from above mentioned Teflon AF 1600, and after sticking a pellicle frame on the front face of the pellicle film pasted up on the frame for preparation through pellicle film adhesives, the pellicle frame was heated with IR lamp and welding of the film was carried out to the pellicle frame. At this time, two frames (the frame for preparation and pellicle frame) were attached in the fixture for immobilization in the condition of having turned the adhesion side of a pellicle frame upward, and they were fixed so that a location might not shift relatively. Subsequently, the frame for preparation located in the outside of a pellicle frame was pulled up, it fixed, and the tension of 0.5 g/cm was given to the film section of a pellicle frame outside.

[0043] Subsequently, moving a cutter along with the periphery of the adhesives part of said pellicle frame using a tube type dispenser for the cutter attached in the SCARA robot, and carrying out per minute 10 microliter dropping of FURORINATO FC75 (Du Pont trade name), cutting removal of the garbage of the film of a pellicle frame outside was



carried out, and the pellicle was completed.

[0044] The pellicle completed [ which was completed and <-pressurization-examined ] was stuck and used as the mask substrate which carried out dust particle inspection beforehand. After setting this in the reduced pressure chamber and decompressing to 500mmHg, it returned to atmospheric pressure again. After returning to atmospheric pressure, the supersonic sensor investigated the restoration time amount of the pellicle film. Furthermore, the foreign matter on a mask substrate (0.3 micrometers or more) was inspected after the experiment. This was carried out 5 times and the result was shown in Table 1. It turned out that the difference with an outside atmospheric pressure was able to be abolished by the pressurization time amount for 10 minutes, without dust invading from this result, even if it used the filter of 0.1 micrometers - 3 micrometer mesh.

[0045]

[Table 1]

[0046] <Escape-of-gas trial> When the pellicle stuck and used as the mask substrate under the fluorescent lamp was further left for 30 minutes, the ambient atmosphere the interior of a room and in a pellicle was sampled and contamination gas concentration was measured, although, as for the interior of a room, about 1 ppm alcohols were detected, as for the inside of a pellicle, only 0.001 ppm alcohols were detected.

[0047] (Example of a comparison) The bleeder with a diameter of 0.5mm was opened in the frame, and the pellicle was produced on the same conditions as said example except the quality of the material having not installed [ dust filtration size ] this as a wrap filter only using the filter for dust removing with a width of face of 9.5mm which is 99.9999% by 0.1 micrometers - 3 micrometers by PTFE, as for the chemical filter.

[0048] The same approach as an example estimated this pellicle. Consequently, when the pellicle stuck and used as the mask substrate under the fluorescent lamp was left for 30 minutes, the ambient atmosphere the interior of a room and in a pellicle was sampled and contamination gas concentration was measured, about 1 ppm alcohols were detected and, as for the interior of a room, 1 ppm alcohols were detected also for the inside of a pellicle.

[0049] While being able to adjust the atmospheric pressure inside a pellicle, without the pellicle equipped with the filter for dust removing and the chemical filter, then dust invading from the above result, it turned out that the contamination gas inside a pellicle was removable.

[0050] In addition, this invention is not limited to the above-mentioned operation gestalt. The above-mentioned operation gestalt is mere instantiation, and no matter it may be what thing which has the same configuration substantially with the technical thought indicated by the claim of this invention, and does the same operation effectiveness so, it is included by the technical range of this invention.

[0051]

[Effect of the Invention] The pellicle of this invention can remove the gas which is enclosed at the time of pellicle attachment and exists in a pellicle while preventing that organic [ from the pellicle outside ] and various inorganic gas invade in a pellicle by using the chemical filter which contains titanium oxide etc. other than the filter for dust removing. Therefore, since generating of the sludge from gas etc. can be prevented also in case it exposes by short wave Nagamitsu (ArF laser, F2 laser, etc.) if the pellicle of this invention is used for the semi-conductor lithography with which short wavelength-ization progresses more, a very detailed pattern can be made to form suitably on a substrate as a result in manufacture of semiconductor devices, such as LSI and a VLSI, etc.

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[Translation done.]

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## CLAIMS

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[Claim(s)]

[Claim 1] The pellicle for lithography which is a pellicle for lithography which comes to paste a pellicle frame the pellicle film at least, and is characterized by preparing the filter for dust removing, and the chemical filter in this bleeder while said pellicle frame has a bleeder.

[Claim 2] The pellicle for lithography according to claim 1 characterized by said chemical filter being a thing containing titanium oxide.

[Claim 3] The pellicle for lithography according to claim 2 to which the chemical filter containing said titanium oxide is characterized by coating with titanium oxide the fiber of the thing which scoured titanium oxide to polytetrafluoroethylene, or an inorganic material.

[Claim 4] The pellicle for lithography given in any 1 term of claim 1 characterized by being what said filter for dust removing becomes from fluororesin, a metal, or the ceramics thru/or claim 3.

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[Translation done.]